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Fate of parabens and 4-hydroxybenzoic acid in aquifer materials columns during step experiments with fresh and sea waters

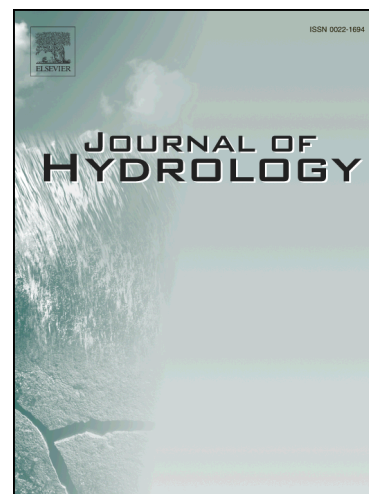C.M. López-Ortiz, N. Boluda-Botella, D. Prats-Rico, I. Sentana-Gadea

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Fate of parabens and 4-hydroxybenzoic acid in aquifer materials columns during step experiments with fresh and sea waters

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Abstract

Coastal areas submitted to seawater intrusion and with discharges from urban and industrial wastewaters, municipal landfill leachates, rivers, recreational waters and other sources are sensitive to be polluted with parabens. Understanding the fate of these compounds in environmental studies, it requires previously the knowledge of the reactive processes in controlled conditions. In this research, laboratory columns experiments were carried out with a group of parabens (methyl-, ethyl-, propyl- and butylparaben) and their main degradation compound (4-hydroxybenzoic acid) to study mainly the dynamic sorption processes in different aquifer materials (100% sand and heterogeneous: 81% sand, 9% silt and 10% clay) and with fresh and sea waters, the end members of seawater intrusions. To the column hydrodynamic characterization, tracer assays with increase and decrease of salinity were performed, to obtain the mean residence time of each column and other transport parameters which allow us to compare parabens´ sorption in different conditions. The results of the adsorption and desorption of parabens in the sand column demonstrated be fast and simultaneous, with a short delay and without influence of the water salinity. Very different results were found in the column experiments with heterogeneous material, where the presence of clay and organic matter increase the time of adsorption/desorption as the length of the alkyl chain paraben increased, according with their hydrophobicity. It should be noted that despite the quick desorption of the major quantities of parabens, the elution of their trace concentrations was very slow (for the seawater, the buthylparaben required a dimensionless time of 800). Planning the restoration of a coastal aquifer with freshwater, and in the conditions of the studied sand column experiment, it will need a dimensionless time of 160. However, it is necessary to take into account that the studied parabens and 4-hydroxybenzoic acid are biodegradable substances, as can

1

be seen in long term experiments, when bacterial proliferation could occur, despite starting the experiment under sterile conditions.

1. Introduction

In terms of chemical structure, parabens are esters of 4-hydroxybenzoic acid, which can be esterified with alkyl substituents ranging from methyl to butyl or benzyl groups. Figure 1 show the structure of the parabens considered in this study: methylparaben (M), ethylparaben (E), propylparaben (P) and butylparaben (B), together 4-hydroxybenzoic acid (H), their main degradation compound.

Figure 1

Błędzka et al., (2014) refers that parabens are widely used as preservatives, mainly in cosmetics (toothpastes, deodorants, skincare creams, bath gels and shampoos) and pharmaceuticals, but also in food commodities and industrial products. These compounds are antimicrobial characteristic with a broad spectrum of activity, low cost, heat stable, effective over an extensive pH range, sufficiently soluble in water to achieve effective concentrations in aqueous media, no perceptible odour or taste and do not induce discoloration (Neidig and Burrell, 1944).

Parabens are lipophilic compounds and their physic-chemical properties depend on the carbon number of the alkyl chain. Table 1 summarizes some physical constants and chemical properties of parabens considered in this study (Lide, 2002; NCBI, 2016; Jewel et al., 2007b; Figueiredo et al., 2016; Soni et al., 2005). The compounds are solid at room temperature and are expected to be essentially non-volatile from water surfaces, due to the low vapour pressures. As the ester chain length increases, water solubility decreases and the octanol/water partition coefficients (log K_{ow}) increase (Elder, 1984). The 4-hydroxybenzoic acid is dissociated at neutral pH, and as a consequence of its acid character, this compound is different to those with basic characteristics. Antimicrobial activity increases according to the length of the chains of the parabens

(Han and Washington, 2005), but generally, microbial replication occurs in water and hence, the amount of paraben dissolved in the aqueous phase and the antimicrobial activity determine the preservative ability.

Table 1

However, these compounds may have harmful consequences for human health (Dagher et al., 2012; Soni et al., 2005; Okubo et al., 2001). Recent reports have indicated that exposure to parabens may modulate or disrupt the endocrine system. Furthermore, due to the high oil/water partition coefficient, if any parabens enter the human body intact, they may be able to accumulate in fatty components of body tissues in a similar manner to that of other lipophilic pollutants that are known to bioaccumulate and they have carcinogenic potential (Darbre, 2004). This researcher referred that parabens are quickly absorbed from the gastrointestinal tract and from blood, hydrolyzed to 4-hydroxybenzoic acid and excreted in the urine, and he provides levels of parabens in foods in the 0.5-2.0 mg/g range, while in pharmaceuticals the concentrations were below 10 mg/g (Soni et al., 2002; Sandanger et al, 2011). Parabens have been detected in human fluids i.e., blood (10 μg/L of methyl-, ethyl- and propylparaben from Sandanger et al., 2011), urine (43.9 μg/L of methyl- and 9.05 μg/L of propylparaben in 96 % of the samples, from Ye et al., 2006), milk (1-8 μg/L of methyl-, 1-1.5 μg/L of propyl- and 1-2 μg/L of butylparaben, from Schlumpf et al., 2010), and human breast tumours (5.1 μg/g of methyl-, 0.5 μg/g of ethyl-, 2.1 μg/g of propyl- and 0.1 μg/g of butylparaben, from Barr et al., 2012) in different populations. Currently, some manufacturers altered composition of their cosmetic products by replacing parabens with other preservative system and introducing so called "paraben free" formulae. In European Union countries, the allowable content of parabens in cosmetic products is 0.4% (4 mg/g) for single ester and 0.8% (8 mg/g) for mixtures of all parabens (Official Journal of the European Union, 2009).

As regards environmental samples, levels of methyl-, ethyl- and propylparaben below 80 ng/L have been measured in rivers (Benijts et al., 2004; Canosa et al., 2006). Concentrations of these compounds in untreated waste waters are below 2500 ng/L, while levels in the effluents of treatment plants are below 100 ng/L. In these samples, propylparaben is considered the main representative of the parabens group (Lee et al., 2005). A great part of the environment input of these compounds is through wastewaters, although agricultural use of fertilizers can also be an important source of parabens because they can lixiviate and contaminate groundwater and aquifers. In addition, they are compounds found in moisturizing, nourishing and

sun creams so another possible pollution route to the environment is by direct bathing, washing or swimming in the waters of rivers, lakes or seas (Núñez, 2010).

Once released into the environment, these compounds will suffer from different processes such as degradation or distribution among the different phases of the system. The role of these processes in the fate of contaminants depends on several variables: *(i)* compound properties *(ii)* water characteristics and *(iii)* system properties. Therefore, it is necessary to understand the behaviour of pollutants in the environment, where they can remain in solution or adsorbed in different types of materials. The sorption process plays a significant role as an attenuation process during subsurface flow as the retention or the release of compounds in the liquid phase, on the solid phase, controls the mobility of the substances in the environment (Limousin et al., 2007). Hence, the investigation of the sorption properties of chemical compounds is mandatory for assessing the environmental behaviour of pollutants in general and, particularly, to assess their potential to leach into the groundwater (Burke et al., 2013). Sorption processes can be driven by diverse mechanisms, including physisorption, chemisorption and mechanical inclusion (Von Oepen et al., 1991). Depending on the characteristics of both sorbent and sorbate, various intermolecular interactions (e.g. Van der Waals interactions, hydrophobic bonding) result in bindings with varying energies. Further, total sorption may be a combination of different sorption mechanisms (Von Oepen et al., 1991) and it is quite difficult to identify each individual contribution to the total. Approaches for estimating the sorption of groundwater contaminants range from theoretical studies (i.e. based on Quantitative Structure - Activity Relationship) to laboratory batch, or column tests to field experiments. The complexity of the approach adopted depends mainly on financial considerations and the degree of uncertainty considered acceptable (Benker et al., 1998).

As regards the laboratory tests, the batch method is the simplest experimental set-up but it is limited by the inappropriate solid/solution ratio used or by the fact that the hydrodynamic conditions of natural porous media are not satisfied (Limousin et al.,2007; Burke et al., 2013). In contrast, column experiments have a distribution of the absorbate in solution / porous medium similar to environmental conditions, and the hydrodynamic characterization of the column can be done with great precision, using suitable tracer substances, as reported in Boluda-Botella et al., 2007, with the ACUAINTRUSION TRANSPORT software. Due to these considerations, some published results reveal that results from batch experiments overestimate the sorption

properties of the studied compounds when compared to those found using column tests (Piatt et al., 1996, Murillo-Torres et al., 2012; Boluda-Botella and Egea-Llopis, 2011).

In column sorption tests, the determination of the hydrodynamic parameters is necessary to adequately explain the behaviour of the different compounds along a column filled with porous media. Different transport parameters such as dispersion can modify the shape of the elution curves for the different solutes present in waters and therefore affect the chemical composition of the groundwater across the flow path in field studies, as reported in Boluda-Botella et al. (2008b).

Sorption isotherms are widely used to characterize retention of chemicals in soils. Simple equations, such as the Freundlich or Langmuir isotherms are commonly used to describe sorption data, although frequently these equations do not accurately describe the data and other more complicated equations are used to adequately describe data (Hinz, 2001).

On the other hand, as mentioned above, there is an important source of parabens in wastewater effluents in coastal areas or by direct release in rivers, lakes or seas, and therefore different water salinity could affect the process of migration and sorption of parabens. The great ionic strength of seawater influences the migration processes of major ions, as studied in laboratory experiments of seawater intrusion (Boluda-Botella et al., 2014) and could have an influence on the physicochemical interactions of parabens compounds, such as the adsorptions or desorption processes.

Therefore, the aim of this paper is the study of the dynamic behaviour of a group of parabens (methyl-, ethyl-, propyl- and butylparaben) and their main metabolite, 4-hydroxybenzoic acid, dissolved in waters of different salinity (fresh and seawater), and in different porous media (sea sand and sand with clay), using laboratory column experiments. The hydrodynamic characterization of the columns will be determined with a tracer in previous assays, with the determination of the mean residence time which permit to compare the evolution of the concentration of parabens in different conditions. Adsorption and desorption are the main reactive processes studied in the step experiments, but other reactive processes could be identifying, if saturation concentration are not achieved or the concentration profile are different to that of the tracer. These results

5

could permit the modelization of the parabens concentration with reactive transport software, to quantify the processes and their dynamic in different conditions and aid to interpret environmental data.

2. Material and Methods

2.1. Characteristics of the column porous media

Two solid materials were used in column experiments: purified commercial sea sand from Merck (Darmstadt, Germany) and natural sediment from Orihuela (Alicante, Spain). The sea sand composition was >90% of particle size 0.100–0.315 mm. This homogeneous medium is called "sand" in this paper and its particle density was determined according to UNE 103-302-94 (AENOR, 1994) obtaining an average value of 2.65 g/cm^3. The natural sediment, previously characterized, was 23.6%, 38.0% and 38.4% sand, silt and clay, respectively, determined by the Bouyoucos hydrometer method, and had 38.3% of $CaCO_3$ and an organic carbon content of 0.78%. The sediment was dried, gently crushed and passed through a 0.45 mm sieve before use. A mixture of 75% (w/w) sea sand and 25% (w/w) sediment was prepared, resulting a heterogeneous medium, called "aquifer material". Its composition was 80.9% sand, 9.5% silt and 9.6% clay and the particle density of this material was 2.62 g/cm^3.

2.2. Waters employed as influent

Fresh and seawaters were used in the experiments. The freshwater (FW) comes directly from the urban water supply of Alicante (from the Taibilla River reservoir) and the seawater (SW) was taken from the Mediterranean Sea (Cala Cantalars, Alicante, Spain). Both fresh and seawaters were sterilised by filtration through a Sterivac GP-10 (Millipore, Bedford) to minimize biodegradation processes. The freshwater was dechlorinated in storage for at least 20 days. The chemical characteristics of the waters employed are summarized in Table 2.

Table 2

2.3. Tracer, reactive compounds and reagents from analytical procedure

Calcium chloride was employed as a tracer; the solution was prepared from anhydrous calcium chloride PA (Panreac). The compounds investigated were methylparaben, ethylparaben, propylparaben, butylparaben and

4-hydroxybenzoic acid (Pharmaceutical secondary standard; traceable to USP and PhEur, Sigma-Aldrich, Steinheim, Germany). The solutions used for the mobile phase in HPLC were: acetonitrile multisolvent for HPLC (Sigma-Aldrich) and ultrapure water from a Milli-Q system (Millipore, Bedford, MA, USA).

2.4. Experimental set-up and tracer test

The experimental set-up consisted of an Omnifit® glass column (21.7 cm length and 1 cm internal diameter) connected to an HPLC pump (Shimadzu LC-9A) with constant rate of 0.5 mL/min. The design of the experimental set-up is shown in Figure 2. The column was filled with sea sand in the first group of experiments and with the aquifer material in the second group.

Figure 2

Tracer test experiments were carried out before starting the reactive studies with parabens, with the purpose of the characterization of the different columns used. The determination of the hydrogeochemical parameters was done by the methodology presented in a previous paper (Boluda-Botella et al., 2010; 2014). $CaCl_2$ prepared in freshwater was employed as tracer, according with experiments carried out by Sardin (1998), in with sand columns and calcareous clay.

The experimental set-up includes an on-line conductivity detector (Shimadzu CDD-6A) which can record conductivity changes in outlet flow each minute, as results of the different tracer concentrations. The employed $CaCl_2$ solution 0.04 M corresponds to 6600 µS/cm, the maximum value reached. The times that the solutions spent in the conductions and conductImeter, before and after the column, were determined in this system, in order to correct the run time of each experiment and to calculate the hydrodynamic characteristics of the column. The determination of this mean time was carried out in the system without column with step tracer input and output, which also allows us to consider the time and dispersion registered in the conductimeter.

On the other hand, to evaluate transport in the adsorption and desorption studies, two different tests with column are used: freshwater resident in the column with tracer input until saturation and after the elution of the tracer with freshwater. The main goal is to compare the elution of parabens with each BTC of the tracer, in

7

both cases: adsorption until parabens saturation, and desorption until total elution of parabens. The final breakthrough curves obtained in the experiments reported conductivity data versus time, taking into account the delay in the conductions and in the conductimeter, and with this consideration, they were employed to determine column hydrodynamic parameters, as will be indicated latter. Table 3 gathers the sequence of the assays carried out.

Table 3

2.5. Parabens adsorption and desorption experiments

After tracer test, the porous media was saturated with freshwater until to achieve the chemical equilibrium. After that, two kinds of assays involving parabens were carried out, using fresh and seawater. The parabens solutions (2 mg/L, approximately, of each substance) were prepared with the respective water, with the aim to perceive changes in the migration of these compounds into the columns submitted to water of different salinity. Formaldehyde was added to prevent biodegradation of the compounds, prior to freshwater, in the case of the sea sand filled column, and prior to seawater, with the aquifer material column.

In these experiments, experimental set-up was simplified and conductivity cell was removed. Time spent in conductions after the column was determined. The eluent was collected in small fractions using fraction collectors (Frac-100 Pharmacia Biotech). Constant flow was controlled during experiments, with the weight of all the water fractions, collected in a given period (Gomis et al., 1997). Simultaneously, the pressure was continuously monitored by a transducer, to perceive changes in system flow. The samples were stored in amber glass vials (40 mL) in a refrigerator at 4º C until analysis, and some of them were analysed, to quantify the parabens and 4-hydroxybenzoic acid concentrations by HPLC-UV.

Constant parabens concentrations (in fresh and seawater) were maintained in the adsorption experiments until the parabens saturation was reached with respect to each component. Afterwards, desorption experiments were conducted with parabens-free waters.

2.6. Determination of hydrodynamic parameters using ACUAINTRUSION TRANSPORT software

The tracer breakthrough curve, obtained in a continuous-flow system, with on-line conductivity measured, and considering the mean time spent in conductions and detector, was input in the ACUAINTRUSION TRANSPORT software. An MS Excel file is required, with conductivity versus experimental time and other input data: length (L) and diameter of column (D), and mean flow rate to obtain the best fit to the BTC. A theoretical breakthrough curve was constructed with the analytical solution of the convection–dispersion equation obtained by Lapidus and Amundson (1952) applied to the experimental data. Additional software characteristics can be found elsewhere (Boluda-Botella et al., 2006, 2014). With this program the following transport parameters were obtained for each scenario: Darcy velocity (u), mean residence time t_m (L/v), longitudinal dispersion coefficient (D_L), Peclet number, ($Pe = vL/D_L$), effective porosity (ε), interstitial velocity ($v=u/\varepsilon$), and dispersivity ($\alpha = L/Pe$).

2.7. Parabens analysis by HPLC-UV

Parabens were determined by High Performance Liquid Chromatography (HPLC), with a liquid chromatograph Agilent 1100 with a UV detector (254 nm). The stationary phase used was an Ascentis RP-Amide 5 µm of 150 mm x 4.6 mm (Sigma-Aldrich, Supelco, Steinheim, Germany) equipped with a pre-column Ascentis RP-Amide 5 µm of 20 mm x 4.0 mm (Sigma-Aldrich, Supelco). The samples (20 µL) were manually injected in the mobile phase, which consisted of a mixture of acetonitrile/water (55:45), at a flow rate 1.0 mL/min. Peak identification was performed by comparison of retention times of standard solutions. Chromatograms obtained for a standard mixture (with fresh and seawater) are shown in Figure 3.

Figure 3

The linearity of the calibration curves was verified by analysis in triplicate of standard solutions containing 0.05, 0.1, 0.3, 0.5, 1.0, 3.0 and 5.0 mg/L for 4-hydroxybenzoic acid and parabens. Table 4 shows the optimum linear range for each compound and the limit of detection found (LOD, calculated as 3 times the standard deviation of the calibration curve and divided by the slope).

Table 4

3. Results

3.1. Characterization of transport through column

Experimental porosity of the medium in the filled column was calculated from the amount of the porous medium and the column volume, resulting in porosity values of 0.400 for sea sand and 0.438 for the aquifer material. On the other hand, calculated porosity and other hydrodynamic and physical characteristics of the filled columns were determined with tracer tests. In these assays, a continuous inflow of $CaCl_2$ in the column permitted the production of conductivity breakthrough curves, as in previous published papers (Boluda-Botella et al., 2010; 2014). Additionally, and as explained previously, in this paper other conductivity breakthrough curves were obtained to find the behaviour of tracers after freshwater inflow into the column, to cause a decrease in conductivity as a consequence of chloride displacement. Table 3 include column tracer (T) experiments and tests called "Experiment without column" (C), with the mean flow and approximate final time of each experiment Other details, about the solutions inflow into the column (FW-T, as freshwater resident and tracer inflow) or porous media (I and II) are explained on the bottom of the Table 3.

Table 5 show the transport parameters of different column experiments by applying ACUAINTRUSION TRANSPORT model to experimental conductivity data versus column time, taking into account the mean time spent in conductions and conductivimeter. These times were 6.4 min in step tracer input and 7.7 min in the tracer output tests.

Table 5

Figure 4 shows the breakthrough curves for the four experiments, (a) and (b) plotted as conductivity measure each minute divided by conductivity maximum for each experiment (Conduct./Conduct. max.) versus dimensionless time (time/t_m), where t_m was the mean residence time determined with the software. The comparison between these breakthrough curves is presented in (c). Experimental data have been used to calculate dimensionless conductivity ($C-C_0/C_f-C_0$), where C_0 is the conductivity at the beginning of the experiment, C_f is the conductivity at the end of the experiment and C is the conductivity determined at each

time. Experimental results are represented using symbols and modelling results, with ACUAINTRUSION TRANSPORT interface, are presented in lines.

Figure 4

This model obtains a good approximation to the experimental data, calculated as the best fit from the four tracer test, with the convection–dispersion equation obtained by Lapidus and Amundson (1952). The experimental breakthrough curves were similar for both columns (sea sand in test I and aquifer material in test II) when dimensionless parameters are considered (Figures 4a and 4b). With respect to displacement experiments (tracer inflow and freshwater inflow to eliminate all tracer concentration), similar BTC have been obtained in dimensionless time. However, the effect of the porous media and the experimental conditions arise when analysing the transport parameters determined with the model (Table 5).

3.2. Study of adsorption and desorption parabens

The adsorption and desorption of parabens through the two different columns were studied, using fresh and seawater. Samples were analysed by HPLC-UV, in order to obtain the parabens concentration curves versus time. The total samples of the experiments were 1254, and the total analysed were 420, distributed as: sand experiments (I): freshwater (321, analyzed 73), seawater (466, analyzed 92); Aquifer experiment (II): freshwater (187, analyzed 127) and seawater (290, analyzed 128). The analysed concentrations of parabens in the inlet solution of adsorption assays are included in Table 6. Experimental data of previous tracer experiments were considered in order to compare adsorption and desorption.

Table 6

3.2.1. Parabens adsorption and desorption through sea sand column by elution with fresh and seawater

Figure 5 show the parabens concentrations of adsorption and desorption with freshwater (a) and with seawater (b), as well as for the tracer. The measured conductivity of tracer experiments is presented as 1.5 x normalized conductivity (dimensionless), which permits to compare easily with respect to inlet and outlet

11

parabens concentrations. Individual paraben concentrations used in the inlet solution were around 2 mg/L, which were maintained for more than 200 minutes.

Figure 5

Adsorption in the sand column with fresh and seawater showed that all the compounds investigated followed identical concentration profile curves to that registered for the tracer, which was slightly earlier than the parabens compounds. No differences among the five compounds were noted, in spite of their different chemical properties (i.e. pKa and Log Kow, Table 1). Similar times in the breakthrough points of fresh and seawaters demonstrated a small influence of ionic strength. Analysing parabens concentrations attained at the plateau with both waters, very small experimental fluctuations were observed, reaching parabens constant concentrations, which were in accordance with the analysed inlet concentrations (Table 6).

Desorption of the different compounds was observed after continuous inlet of parabens-free freshwater and seawater. In general, the behaviour of all parabens was similar to that of the tracer, with identical concentration profiles and no significant variation among the compounds tested. Again a slight delay was noted for all concentration profiles of parabens with respect to that of the tracer, and the delay in both cases was greater than that of the adsorption experiments. A slight decrease of the concentration was noticed for 4-hydroxybenzoic acid in the seawater experiment, just before desorption process started and prior to the tracer decreasing. The reason for this decrease is not known, although a possible explanation could be related to biodegradation. In the seawater experiment, a previous treatment of the column with formaldehyde was not carried out (Table 3), and hence, growth of microorganism could be developed.

3.2.2. Parabens adsorption and desorption through aquifer material column by elution with fresh and seawater

As regards the experiments carried out using the aquifer material (Figure 6), adsorption with freshwater (a) and saline water (b) present differences when the curves of each compound are compared.

Figure 6

The results show that the adsorption time of the analytes was higher than that of the tracer, and increased with the alkyl chain length of the compounds, or in other words, as the hydrophobicity of the compound increased (Table 1). The 4-hydroxybenzoic acid, the most polar member, shows a short elution time, probably as a consequence of the pH of the waters employed and its pKa value. Methyl and ethylparaben behaved similarly and needed more time for the tracer to achieve complete adsorption. Greater adsorption time was observed for propyl and butylparaben. Results of the adsorption in the seawater intrusion experiment were qualitatively similar to those encountered in the freshwater experiment, showing a longer time for the butylparaben. As a consequence of the parabens adsorption studies in aquifer materials, the hydrophobicity of the compound has a great influence in the sorption processes, due to the presence of clay and organic matter, with a longer time in the seawater, being the longest for the butylparaben.

As regards the desorption profiles, a reduction of the maximum concentrations of 4-hydroxybenzoic acid was noted before the tracer concentration diminished, in the freshwater assay. This effect also occurs to a lesser extent for the methylparaben, just at the beginning of desorption experiment, and before the elution time of the tracer. As mentioned earlier, these differences could be due to biodegradation of the compound, due to bacterial growth in the porous medium used, sand in this case, since it was not sterilized and formaldehyde was not added before the test was carried out (Table 3). Desorption to the other compounds with freshwater was delayed to that of the tracer, and with similar behaviour for all parabens studied of desorption with seawater. The elution of the tested compounds has a clear chromatographic sequence, in line with the hydrophobic characteristics. Differences between freshwater and seawater desorption are evaluated in the next section..

3.2.3. Desorption of trace levels of parabens

Long-time elution of parabens has been detected in all the experiments, and a study of the trace concentrations is presented. The times of elution were determined taking into account the quantification limit of 0.1 mg/L in HPLC analysis. In the case of sand column, all the compounds showed the same time with fresh and seawater, near 25 minutes, according with previous results, without influence of ionic strength in sand column. However, different times were determined for all compounds eluted in fresh and seawater in the aquifer material column: 4-hydroxybenzoic acid (24 and 30 minutes), methylparaben (29 and 40 minutes),

13

ethylparaben (34 and 47 minutes), propylparaben (1 hour in both cases) and butylparaben (2 and 2.5 hours). A small effect of ionic strength is reflected in the data from aquifer material, and never effect of the salinity in sand columns.

Another interesting result is the appearance of trace levels of parabens (minor of the detected limit) at long elution times. The sand columns experiments registered more than 40 hours when freshwater was used and more than 90 hours with seawater. This very long elution times contrast with the previous and in this case, the effect of the ionic strength in sand was remarkable. On the other hand, and according with the previous study of the traces, the elution of paraben traces in aquifer columns required different times for all compounds. Traces of butylparaben (the most retained compound) were found more than 40 hours with freshwater and 200 hours with seawater, so salinity has a great influence on the parabens desorption in small concentration.

3.2.4. Comparison of parabens adsorption and desorption through columns with different filling materials

In order to compare adsorption and desorption curves in experiments, plots of parabens concentrations versus dimensionless time (corresponding to time/t_m, and also known as pore volume) are included in Figure 7. Tracer corresponding to sand (Tracer-S) and aquifer material (Tracer-A) are shown in the same figure.

Figure 7

Adsorption studies carried out with the sand column (S) showed small experimental differences between fresh (S-FW) and seawater (S-SW) and for all components (H, M, E, P, B), with a small delay with respect to the tracers. A clear evolution can be observed in adsorption studies with the aquifer material columns (A) showing different results for each compound. The increase in the length of the chain of the parabens provoked an increase of the delay with respect to the tracer, and comparing the influence of different types of waters, the longest compounds are several differences for saline water (A-SW) with respect to freshwater (A-FW). Analysing in the columns desorption with two types of waters, a long tail is observed with the aquifer material column in the longest compounds, although for 4-hydroxybenzoic acid, this effect was not significant.

Biodegradation processes are noteworthy in desorption experiments in p-4-hydroxybenzoic acid (H) and methylparaben (M), in the cases of the sand column with seawater (S-SW) and the aquifer material column with freshwater (A-FW). The long-chain compounds are not affected by this process. Analysing desorption in both columns and two types of water in the case of ethylparaben (E), the curves have similar dimensionless time (near to 2) in the point of the greatest slope, and similar to M in profiles of experiments without degradation. However a long tail is observed for saline water with the aquifer material column for M and E.

Differences between desorption of the longest compounds, propylparaben (P) and butylparaben (B) with respect to the previous one can be clearly observed. The salinity of the water has a minor influence on the elution of these parabens with respect to the column material, where presence of clay and organic fraction of sediments induces a slower elution of parabens, with a very clear delay.

4. Discussion

4.1. Breakthrough curves and transport column parameters

The tracer breakthrough curves (BTCs) of the column, determined with on-line conductimeter date and taking into account the time spent in conductions and detector, were used to obtain the hydrodynamic parameters with ACUAINTRUSION TRANSPORT interface, which are according with the experimental porosities. The BTCs of the tracer test, with increase and decrease of conductivity, plotted in dimensionless time and conductivity were similar, contrarily to previous non-published assays in columns with greater diameter.

Mean residence times were similar in all cases and ranged from 13.2 to 15 minutes (Table 5), with slightly lower values for the sand filled column with tracer displacement (T-FW-I), where a large flow was registered, and hence great interstitial velocity was determined, as a combined effect with the small effective porosity (0.40). This experimental breakthrough curve is in advance of the other T-FW-II, with greater t_m and effective porosity.

Transport in the columns was more affected by advection than diffusion, as the determined Peclet number was higher or near 50, and, therefore, dispersivities (α) were calculated as L/*Pe*. The calculated dispersivity values ranged from 0.25 to 0.44. In a previous paper, using columns with lengths in the 22 to 22.4 cm range

15

and 2.5 cm internal diameter, dispersivities lower than 0.45 corresponded to hydrodynamic flow characteristics similar to plug flow (Boluda- Botella et al., 2010). In the present research, the column was 21.7 cm length and the small dispersivities reported are in the range of that obtained previously.

The calculated Peclet number (Pe) of each experiment ranged from 49 to 86, and were slightly higher in the sand column with respect to the aquifer material column. A greater Peclet number was registered in the cases of the tracer displacement with freshwater (T-FW-I), in contrast to other unpublished previous studies that were carried out with wider columns than this research (2.5 cm internal diameter in previous and 1 cm in the present paper). The small Pe and as consequence, the big dispersion observed when calcium chloride decreasing was probably by the transversal dispersion or other processes related with the hydrodynamic on the big column diameter.

The small columns used in this research allow us to realize column studies more quickly than previous studies (tracer test of 15 minutes as opposed to nearly 2 hours in larger columns). On the other hand, similar hydrodynamic characteristics, such as mean residence time, in experiments with increased and decreased of tracer concentration were obtained. This is a consequence of the studies of tracer assays without column, which obtain different times spent in conductions, longer when conductivity diminishes (7.7 min, with respect to 6.4 min, when conductivity increased), and yielding a final time spent in the column (without conductions), similar in both cases, as shown in Table 5.

The experimental porosities shown in the previous section (0.400 of sand and 0.438 of aquifer material) are in line with the calculated effective porosities with the model (0.40 and 0.42 respectively). Identical experimental and effective porosity was determined in sand but the presence of clay diminishes the effective porosity, probably due to the formation of non-accessible pores, when the aquifer material is used. On the other hand, comparing the two porous media, a lower median grain size increased the water-storage capacity (Stephens et al., 1998), as can be seen in the aquifer material column, and in previous LAS studies (Boluda-Botella et al., 2010). Qahman and Larabi (2005) in the study of the seawater intrusion in Gaza aquifer referred a porosity of 0.40. Other papers are flow rates in the range or greater as presented in this research: Russak et al., (2016) in the study of trace elements (Li, B, Mn and Ba) as sensitive indicators for salinization and

freshening events in coastal aquifers used a flow rate of about 1 mL/min in the laboratory experiments, double the flow rate employed in this paper; Chang and Clement (2012), in the regional flux experiments used a velocity of 0.832 cm^3/s, a hundred times the employed (0.5 mL/min). With respect to employed columns in this paper, other laboratory experiments used column with 7 cm length and 1 cm internal diameter, lesser that our column and with the same diameter (Nsir et al., 2014), when pressure drop was negligible and the wall effect are not considered, as the present research.

In conclusion, the model obtains a good fit to the experimental data of each test. The differences between tracer test are consequence of the experimental conditions (flow) and porous media (porosity), which can be compared considering dimensionless time and conductivity. Determination of the time spent in conductions, longer when tracer displacement test is carried out, allows us to calculate the mean residence time exactly. The BTCs shown small differences, having different chemical composition and in assays with different salinity of the resident water (freshwater or saline tracer solution). The transport parameters determined by the model for each experiment are according with experimental porosity, with previous column experiments in columns with greater internal diameter and with other published researches of laboratory and field. The small mean residence time compared with previous research allows us to carry out shorter tests with this Omnifit® glass column, when plug flow conditions are achieved and with conditions to reach great variations of concentration, as occurs in seawater intrusion experiments (Boluda-Botella et al., 2008b).

4.2. Study of adsorption and desorption parabens

As has been shown, the adsorption and desorption processes of the studied parabens in sandy material are very fast and similar to the tracer. In contrast, other organic compounds such as methylene blue were strongly retained by the sand as has been previously reported (Varlikli et al., 2009). With respect to the behaviour of the studied parabens in the aquifer material, the elution has a clear chromatographic sequence, in line with a hydrophobic mechanism. This fact is according with the studies in field tests developed in the saturated zone by Krueger et al., (1998a, 1998b), which presented a chromatographic separation of the Linear Alkylbenzene Sulphonate (LAS) homologues from a surfactant mixture, with a delay of the longer alkyl chain homologues during transport. Other studies of LAS desorption carried out in column experiments showed the same behaviour previously described (Boluda-Botella et al., 2008a). On the other hand, column experiments and

17

field tracer test showed that LAS biodegradation was preferential in the longer-chain LAS homologues (Krueger et al., (1998b)). Both process, sorption and biodegradation act simultaneously and it is difficult to evaluate each process separately, with the increased of the complexity in environmental conditions, with other processes involved. The main focus of this research was sorption processes, but biodegradation processes are present if the porous medium is not previously sterilized, as was observed in desorption experiments in p-4-hydroxybenzoic acid (H) and methylparaben (M), in the cases of the sand column with seawater (S-SW) and the aquifer material column with freshwater (A-FW). The biodegradation of the shorter- chain compounds contrast with the results of Krueger et al., (1998) of field tests with continuous LAS input, when preferential biodegradation of the longer-chain LAS homologues occurs.

With respect to the long time of desorption of trace levels of parabens, and taking into account a mean residence time of around 15 minutes, the seawater in sand and aquifer columns spent respectively 360 and 800 dimensionless time (pore volumes or times the elution of tracer), so to provoke the elimination of the adsorbed parabens in a sandy aquifer, with 10% clay, the elution of the seawater volume corresponding to 800 times the volume occupied in a coastal aquifer will be required. Estimating the freshwater volume implicated in the restoration of a sandy aquifer polluted with trace concentrations of parabens, 160 times the water volume occupied in this area will be necessary. Thus, the sorption of parabens is great at tracer concentrations and enhanced due to the higher ionic strength of the seawater. As has been shown previously (Bui and Choi, 2010) the ionic strength of the solution influenced the sorption characteristics of some pharmaceuticals, although the results depended on the composition of the solution and the chemical characteristics of the adsorbates. It should be noted that the high values in pore volume (or dimensionless time), as 160 or 800, contrast with respect to 3, the dimensionless time of the point of the most slope concentration variation, when the concentration diminished abruptly.

In future researches, the modelization of these dynamic experiments could be carried out with a reactive transport such as PHREEQC (Parkhurst and Appelo, 1999), similarly to LAS pulses (Boluda-Botella and Egea-Llopis, 2011). The desorption of continuous LAS in sand and soil columns (Boluda-Botella et al., 2008a) demonstrated a long elution of the longer alkylic chains (C_{12} LAS and C_{13} LAS), with more dispersive spreading in the case of soil columns, and with greater differences with the experimental data and modelled results. Probably the studies of desorption experiments should be compared with the tracer test, where their

concentration is decreased, as the present study. Other important future research is in the way of the biodegradation conditions, as mechanism of elimination of parabens.

5. Conclusions

The exact determination of t_m (mean residence time) of the column with tracer experiments permits the comparison between different assays in dimensionless time (or pore volume), when tracer concentration increased or decreased, which present similar transport parameters.

The methylparaben (M), ethylparaben (E), propylparaben (P) and butylparaben (B), together 4-hydroxybenzoic acid (H) followed identical concentration profile in the sand column, with a slight delay with respect to the tracer, and without differences in fresh and seawaters. The studies in aquifer material showed a clear evolution in the parabens adsorption and desorption, as the increase in the length of the chain of the parabens provoked an increase of the delay with respect to the tracer: The mechanism could be hydrophobic interactions, favoured by the presence of clay and organic matter, and with influence of the salinity in the elution of the longest compounds.

The analysis of trace concentration in desorption with a quantification limit of 0.1 mg/L demonstrated a small effect of ionic strength in the data from aquifer material, and never effect of the salinity in sand columns. However, salinity has a great influence on paraben desorption in trace levels of parabens (minor of the limit of detection) at long elution times. The sand columns experiments registered more than 40 hours when freshwater was used and more than 90 hours with seawater. The elution of paraben traces in aquifer columns required different times for all compounds, and for butylparaben, the most retained compound, the elution reached 800 dimensionless time (or pore volumes) Estimating the freshwater volume implicated in the restoration of an aquifer polluted with trace concentrations of parabens, 160 times the water volume occupied in this area will be necessary.

Simultaneously to the sorption, the biodegradation processes should take into account as an important elimination process, preferentially to the smallest compounds, in contrast to field tests with continuous LAS input, when biodegradation of the longer-chain LAS homologues was found.

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21

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Table 1. Physical constants and chemical properties of 4-hydroxybenzoic acid and parabens considered in this studio from Handbook of Chemistry and Physics (Lide, 2002) and other authors

Chemical names	4-hydroxybenzoic acid	Methyl p-hydroxybenzoate	Ethyl p-hydroxybenzoate	n-Propyl p-hydroxybenzoate	n-Butyl p-hydroxybenzoate
Short name in this study	H	M	E	P	B
Molecular formula	$C_7H_6O_3$	$C_8H_8O_3$	$C_9H_{10}O_3$	$C_{10}H_{12}O_3$	$C_{11}H_{14}O_3$
CAS Registry Number	99-96-7	99-76-3	120-47-8	94-13-3	94-26-8
Molecular weight (g/mol)	138.12	152.15	166.17	180.20	194.23
Melting point (ºC)	214.5	131	117	97	68.5
Boiling point (ºC)	336[d]	275	297.5	294[d]	309[d]
Vapor Pressure (mm Hg at 25 °C)[a]	$1.9 \ 10^{-7}$	$2.37 \ 10^{-4}$	$9.29 \ 10^{-5}$	$5.55 \ 10^{-4}$	$1.86 \ 10^{-4}$
Density (g/cm³) at t (ºC)	1.46^{25}			1.063^{102}	
Water solubility at 25 °C (g/100 mL)[b]	0.5	0.2	0.086	0.030	0.015
Log Kow[c]	1.33	1.67	2.03	2.55	3.00
pKa[d]	4.57	8.17	8.22	8.35	8.37

[a] Data from NCBI, 2016

[b] Data from Jewel et al. (2007b)

[c] Values from Chemspider (Figueiredo et al., 2016)

[d] Data from Soni et al. (2005)

Table 2. Chemical characteristics of the waters employed throughout the work (FW, fresh water, SW, seawater).

Parameters	FW	SW
pH	8.1	8.3
Na^+ (mg/L)	80	11700
K^+ (mg/L)	2	420
Ca^{2+} (mg/L)	70	550
Mg^{2+} (mg/L)	40	1400
Cl^- (mg/L)	190	21000
SO_4^{2-} (mg/L)	90	3000
HCO_3^- (mg/L)	188	120
F^- (mg/L)	0.26	2.3
Br^- (mg/L)	0.12	80

Table 3. General description of column experiments.

Assay nomenclature[#]	Porous medium	Resident solution	Injected solution	Mean flow (mL/min)	Final time (min)
FW-T-I	100% Sea Sand	Freshwater	Tracer	0.486	49
T-FW-I	100% Sea Sand	Tracer	Freshwater	0.509	56
C-FW-T-I	Experiment without column	Freshwater	Tracer	0.486	10
C-T-FW-I	Experiment without column	Tracer	Freshwater	0.485	20
Formaldehyde addition	100% Sea Sand	Freshwater	Formaldehyde	0.484	15
Formaldehyde removal	100% Sea Sand	Formaldehyde	Freshwater	0.491	30
FW-P_{FW}-I	100% Sea Sand	Freshwater	Parabens freshwater	0.489	235
P_F-FW-I	100% Sea Sand	Parabens freshwater	Freshwater	0.484	2480
FW-P_{SW}-I	100% Sea Sand	Freshwater	Parabens seawater	0.502	265
P_{SW}-SW-I	100% Sea Sand	Parabens seawater	Seawater	0.481	4042
SW-FW-I	100% Sea Sand	Seawater	Freshwater	0.471	535
FW-T-II	Aquifer Material	Freshwater	Tracer	0.471	100
T-FW-II	Aquifer Material	Tracer	Freshwater	0.484	142
C-FW-T-II	Experiment without column	Freshwater	Tracer	0.468	20

C-T-FW-II	Experiment without column	Tracer	Freshwater	0.467	25
FW-P_{FW}-II	Aquifer Material	Freshwater	Parabens freshwater	0.465	414
P_F-FW-II	Aquifer Material	Parabens freshwater	Freshwater	0.471	2445
Formaldehyde addition	Aquifer Material	Freshwater	Formaldehyde	0.468	15
Formaldehyde removal	Aquifer Material	Formaldehyde	Freshwater	0.486	30
FW-P_{SW}-II	Aquifer Material	Freshwater	Parabens seawater	0.498	295
P_{SW}-SW-II	Aquifer Material	Parabens seawater	Seawater	0.470	12550
SW-FW-II	Aquifer Material	Seawater	Freshwater	0.491	33

[#]Tracer (T), Experiment without column (C), Freshwater (FW), Seawater (SW), Parabens (P), Experiment with sea sand (I) and Experiment with aquifer material (II).

Table 4. Calibration parameters of the HPLC-UV method used for the determination of parabens

Water type	FRESHWATER				
Compound	H	M	E	P	B
Range (mg/L)	0.15-5	0.11-5	0.19-5	0.17-5	0.21-5
Intercept	1.3 ± 3.4	-8 ± 6	-17 ± 16	-5 ± 4	-5 ± 4
Slope	95.1 ± 1.3	148 ± 3	145 ± 6	132 ± 1	113 ± 1
r^2	0.9999	0.9999	0.9999	0.9999	0.9999
LOD (mg/L)	0.045	0.033	0.058	0.051	0.064
LOQ (mg/L)	0.15	0.11	0.19	0.17	0.21

Water type	SEAWATER				
Compound	H	M	E	P	B
Range (mg/L)	0.16-5	0.063-5	0.11-5	0.24-5	0.25-5
Intercept	1 ± 4	1 ± 2	1 ± 4	-1 ± 8	1 ± 7
Slope	103 ± 1	155 ± 1	148 ± 1	137 ± 3	109 ± 2
r^2	1	1	0.9999	0.9999	0.9999
LOD (mg/L)	0.048	0.019	0.034	0.072	0.076
LOQ (mg/L)	0.16	0.063	0.11	0.24	0.25

Table 5. Transport parameters of different column experiments: Darcy velocity (u), mean residence time tm (L/v), longitudinal dispersion coefficient (D_L), Peclet number, (Pe = vL/DL), effective porosity (ε), interstitial velocity (v=u/ε), and dispersivity (α = L/Pe). They have been obtained by applying ACUAINTRUSION TRANSPORT model to experimental conductivity data versus column time.

	Test			
Parameter	**FW-T-I**	**T-FW-I**	**FW-T-II**	**T-FW-II**
Flow (mg/min)	486	509	471	484
Pe (*vL/D*)	70	86	49	62
t_m (min)	14.4	13.2	15.0	15.0
u (cm/h)	37	39	36	37
Effective ε	0.40	0.40	0.42	0.42
v (cm/h)	91	97	87	89
D_L (cm^2/h)	28	24	38	31
α (cm)	0.31	0.25	0.44	0.35

29

Table 6. Parabens concentrations in the inlet solution for adsorption experiments

	Compound				
Experiment	**H**	**M**	**E**	**P**	**B**
FW-I	2.2	1.9	2.0	1.9	1.9
SW-I	1.8	1.8	1.8	1.8	1.7
FW-II	2.0	1.3	1.9	1.7	1.8
SW-II	1.8	1.6	1.7	1.7	1.8

Freshwater (FW), Seawater (SW), Experiment with sea sand (I) and Experiment with aquifer material (II), 4-Hydroxybenzoic acid (H), methylparaben (M), ethylparaben (E), propylparaben (P) and butylparaben (B).
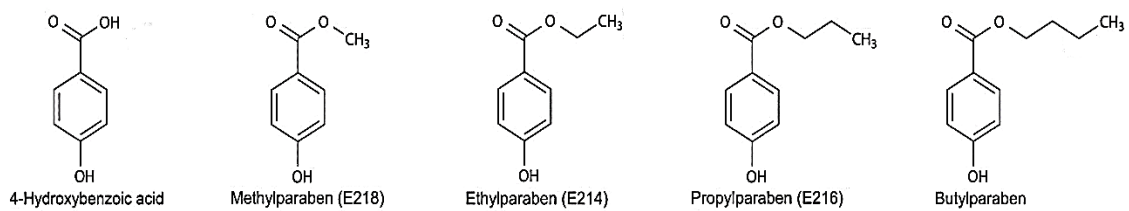
Figure 1. Structure of the different compounds considered in the present study.
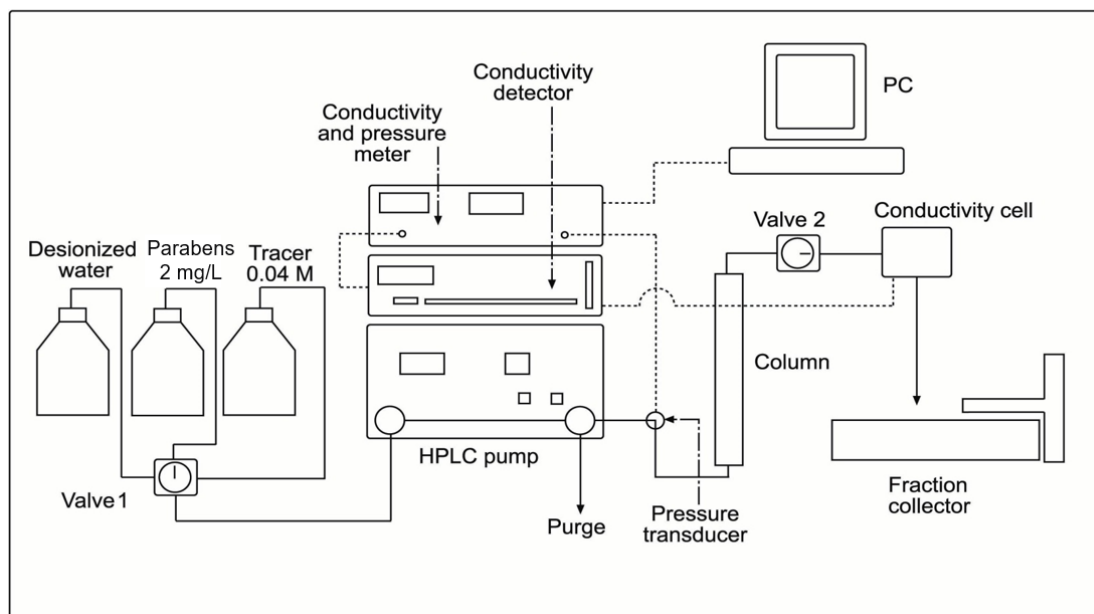
Figure 2. The scheme of the experimental set-up utilized in column experiments
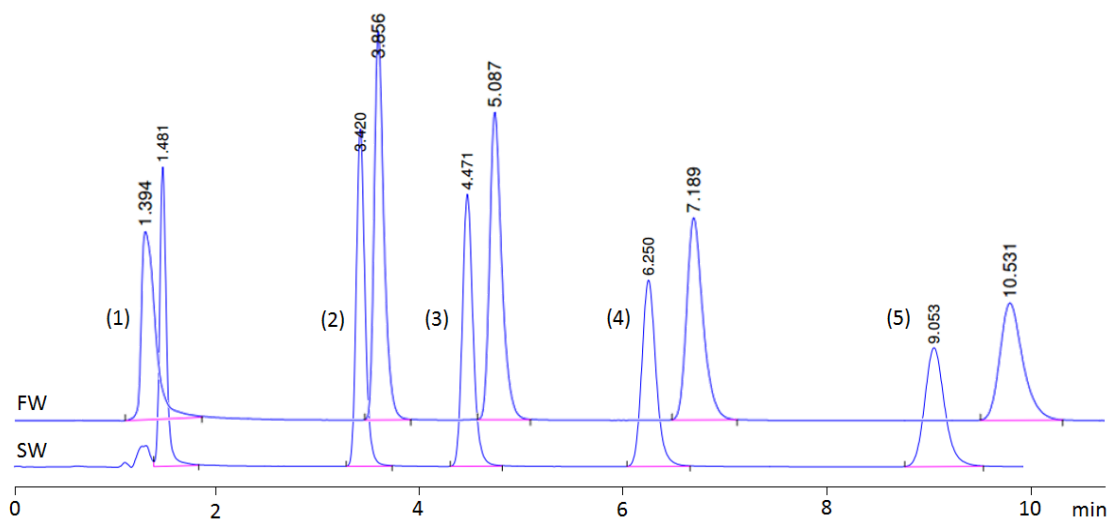
Figure 3. Chromatographic parabens profile in freshwater (FW) and seawater (SW). (1) 4-hydroxybenzoic acid, (2) methylparaben, (3) ethylparaben, (4) propylparaben, (5) butylparaben.
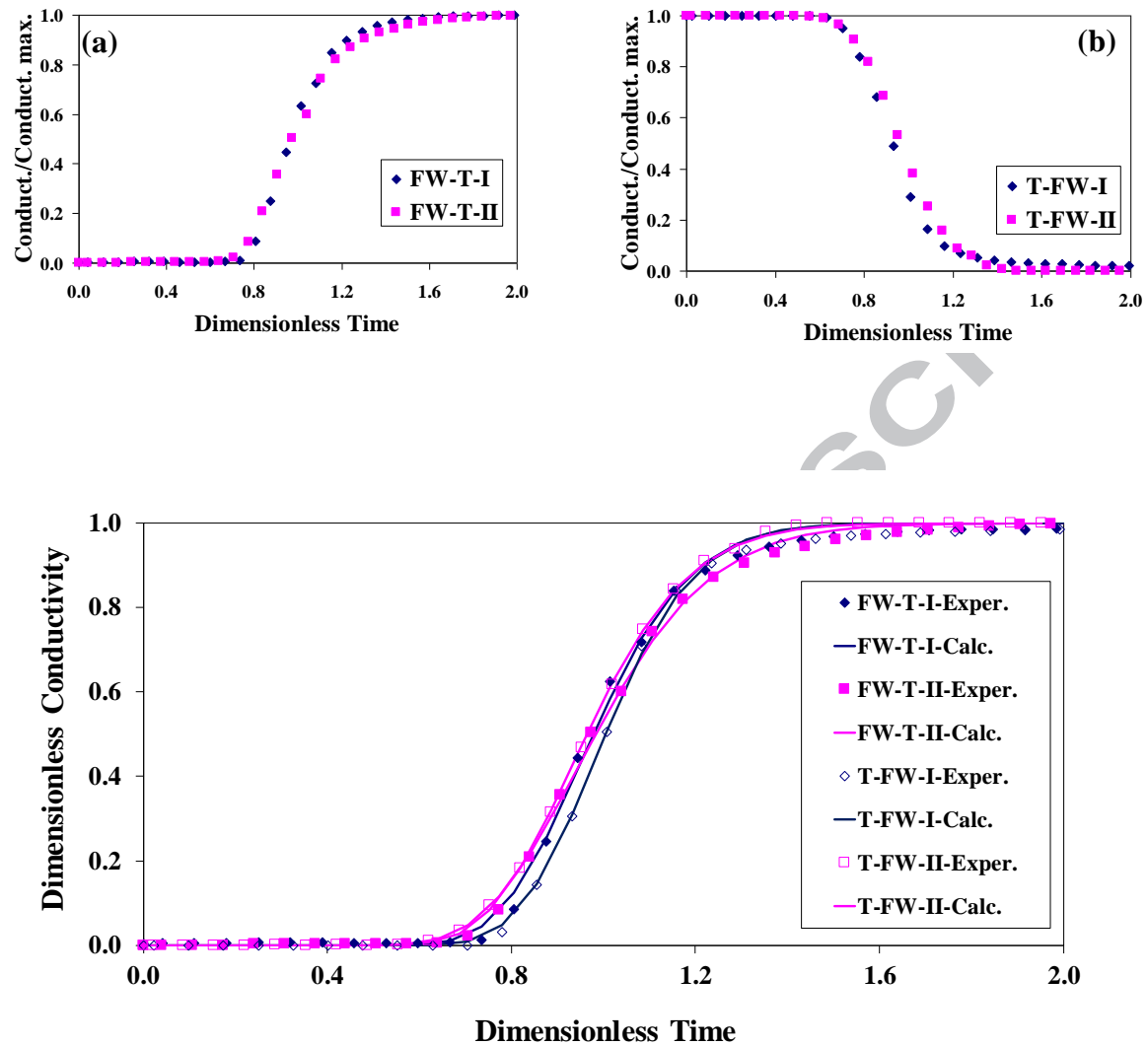
33

Figure 4. Tracer breakthrough curves plotted as (Conductivity/Conductivity maximum) versus dimensionless time (time/t_m) carried out with: (a) Step tracer input; (b) Tracer displacement with freshwater. (c) Experimental tracer breakthrough curves in dimensionless conductivity ($C-C_0/C_f-C_0$) vs. dimensionless time. Lines correspond to modelled breakthrough curves with ACUAINTRUSION TRANSPORT interface. Standard uncertainties u are u(time) = 15 s, u(dimensionless time) = 0.02 and u(dimensionless conductivity) = 0.01.
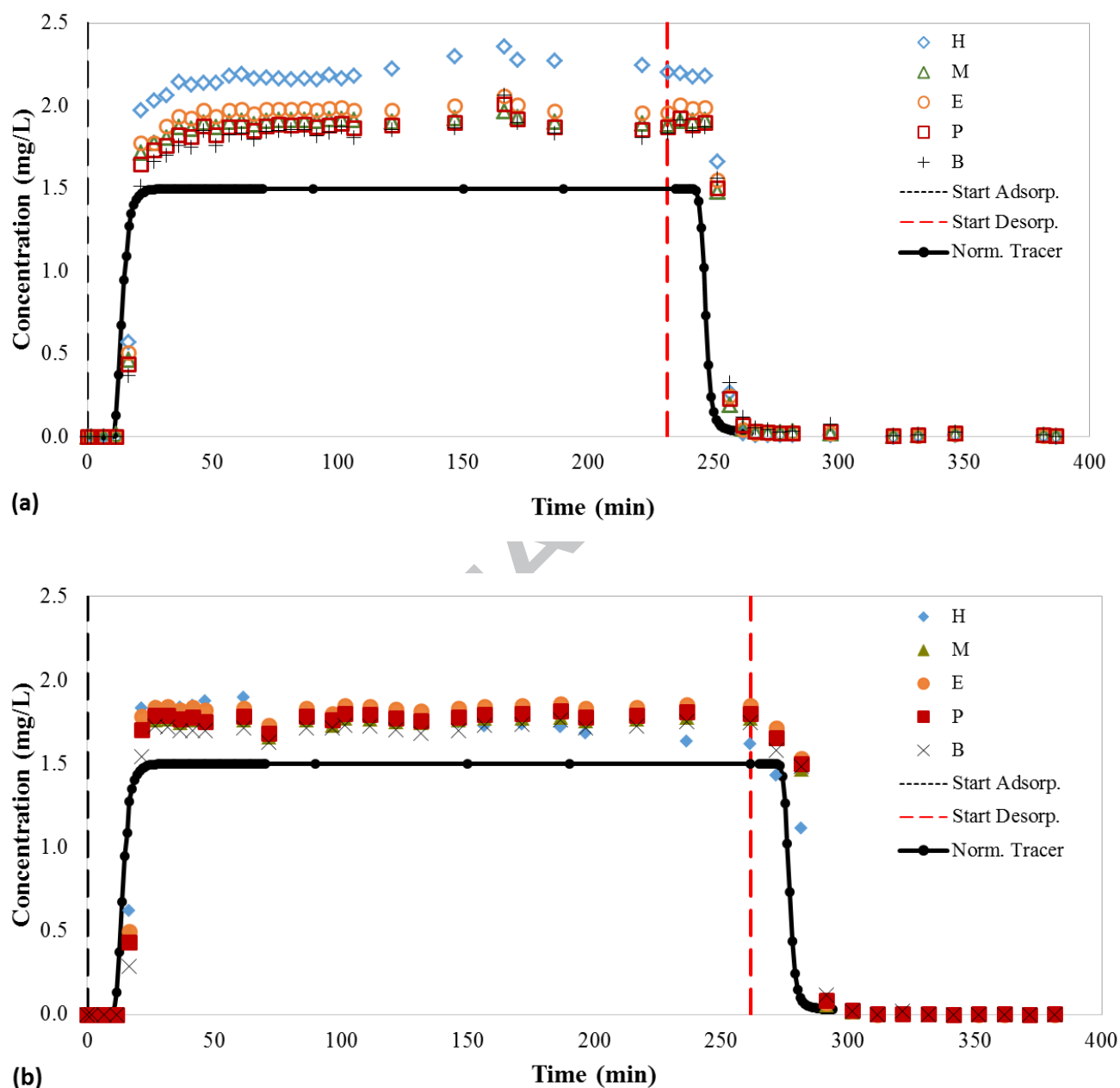
Figure 5. Evolution of concentrations of 4-Hydroxybenzoic acid (H), methylparaben (M), ethylparaben (E), propylparaben (P) and butylparaben (B) in sea sand column. (a) Experiments using freshwater, (b) Experiments using seawater. Normalized conductivities of the tracer (x1.5) correspond to data Norm. Tracer. Standard uncertainties u are u(time) = 2.5 min, u(H and B concentration) = 0.1 mg/L and u(M, E and P concentration) = 0.05 mg/L.
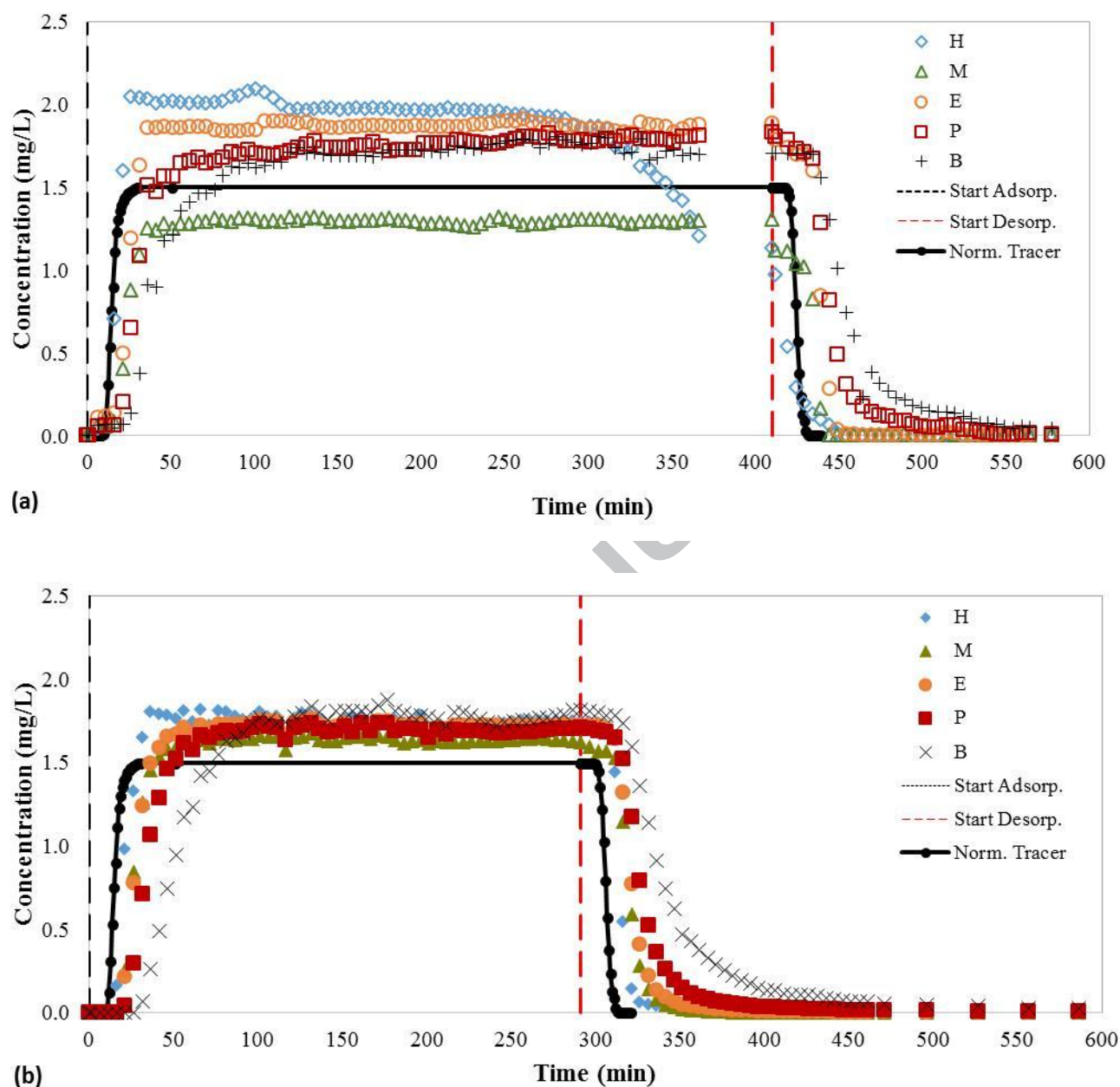
Figure 6. Evolution of concentrations of 4-Hydroxybenzoic acid (H), methylparaben (M), ethylparaben (E), propylparaben (P) and butylparaben (B) in aquifer material: (a) Experiments using freshwater, (b) Experiments using seawater. Normalized conductivities of the tracer (x1.5) correspond to data Norm. Tracer. Standard uncertainties u are u(time) = 2.5 min, u(H and B concentration) = 0.1 mg/L and u(M, E and P concentration) = 0.05 mg/L.

37

Figure 7. Concentration profile of 4-Hydroxybenzoic acid (H), methylparaben (M), ethylparaben (E), propylparaben (P) and butylparaben (B) during the adsorption experiments (left column) and the desorption experiments (righ column). AM, aquifer material; S, sand; FW, freshwater; SW, seawater. Standard uncertainties u are u(dimensionless time) = 0.2, u(H and B concentration) = 0.1 mg/L and u(M, E and P concentration) = 0.05 mg/L.

38

- Sorption (adsorption and desorption) of parabens in laboratory sand columns with fresh and seawater present the same elution curves.

- Sorption of parabens in the sand column was fast and simultaneous, with small delay with respect to the tracer.

- Sorption of parabens in the sandy column, with 10 % of clay content, presents a delay of parabens according to the length of the alkyl chain.

- Sandy aquifers with presence of clay and polluted with parabens traces will need a restoration for long-time

- The biodegradation of the shorter- chain compounds of parabens is favoured, contrarily to other organics as LAS (Linear Alkylbenzene Sulphonate) homologues.